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(21) International Application No.: PCT/CH94/00159  (22) International Filing Date: August 5, 1994 (8/5/94)  (30) Priority: 2359/93-6 August 6, 1993 (8/6/93) Switzerland  (71) Applicant ( <i>for all contracting nations except the United States</i> ): La Marina Patent Holding S.A. (Panama/Panama); Urbanizacion Obarro Torre Swiss Bank, 16 <sup>th</sup> floor, 53 <sup>rd</sup> Street, Panama (PA)  (72) Inventor; and (75) Inventor/ Applicant ( <i>only for the United States</i> ): Erna Eichenberger (Switzerland/Spain), Carrer del Rascio 41, Costa Nova Marina, E-03730 Javea (Spain)  (74) Attorney: Isler & Pedrazzini AG, P.O. Box 6940, CH-8023 Zurich (Switzerland)		(81) Contracting nations: Australia, Brazil, Canada, Japan, Norway, U.S. Patent; European patent (Austria, Belgium, Switzerland, Germany, Denmark, Spain, France, Great Britain, Greece, Ireland, Italy, Luxemburg, Monaco, Netherlands, Portugal, Sweden)  <b>Published</b> <i>with the International Search Report before expiration of the period allowed for changes in the claims; publication to be repeated if there are changes</i>
(54) Title: <b>PHOSPHATE- AND CHLORINE-FREE DETERGENT</b>  (57) Abstract  The novel environmentally friendly products based on washing-active, non-ionogenic and/or anionic surface-active substances also contain amphoteric tensides and citric acid or its salts and other auxiliary substances. Since these products are highly active, they may be used sparingly for washing both textiles and dishes.		

## PHOSPHATE- AND CHLORINE-FREE DETERGENT

With increasing environmental concerns on the part of the population, there has also been an increasing demand on the part of the public for a detergent that has an excellent detergency but is safe for the environment. Likewise, there has also been a great increase in demands by legislators with regard to regulations to protect bodies of water.

Various products commercially available today are advertised as "environmentally friendly" or "ecological". However, on closer analysis, most of these products do not conform to the statutory standards or they do not yield the desired washing results.

Therefore, one object of this invention was to develop a detergent that is free of phosphate and chlorine but also does not give rise to any other unwanted water pollution, while at the same time meeting all the demands of housewives with regard to protecting fabrics, cleaning power, spot removal, etc. in machine laundry as well as hand laundry.

Another object of this invention was to produce a phosphate- and chlorine-free detergent for dishwashing machines that would also meet all the requirements of water conservation while having the required detergent activity in order to remove all the soiling from plates and utensils without leaving any residue and without attacking the dishes and utensils.

Both of these objects have surprisingly been achieved by a suitable new combination of known compounds.

The phosphate- and chlorine-free detergent and dishwashing products according to this invention are defined in Claim 1.

A preferred composition for such a textile detergent also contains, in addition to the wash-active substances and citric acid, a component that enhances detergent power (activator), alkali carbonates to adjust the desired pH, alkali silicates, sequestering agents, optical brighteners, enzymes and optional coloring agents and perfume.

A combination of amphoteric and nonionic and/or anionic surface-active substances are suitable as the wash-active substances for textile detergents. For example, preparations based on sodium lauryl sulfates such as the commercial product "Texapon" (Henkel AG) or natural soaps such as primary soap or mixtures thereof may be used as the anionic surface-active substances. Known products based on ethoxylene or higher fatty alcohols such as the Lutensols of BASF and others as well as fatty alcohols may be used as the nonionic surface-active substances. Suitable amphoteric surface-active substances include the products sold under the brand name Ampholak by Berol Nobel AB. The wash-active substances are advantageously present in a total amount of 10-50 percent by weight in the textile detergent according to this invention. Thanks to this combination of wash-active substances, the detergent power of the product does not depend on the washing temperature; this is all the more true since there is no bleaching component which does not manifest its effect until reaching elevated temperatures such as above 60°C.

NTA may optionally be added, in particular in the form of its trisodium salt such as the product available as Trilon from the company BASF in an amount of up to 10 percent by weight. It replaces the phosphates used previously while also acting as an antioxidant.

Citric acid or the salts thereof can be mentioned as an additional important component. In an amount of 1-20 percent by weight it ensures the good solubility of the detergent while also acting as a sequestering agent.

The activator component preferably contains borates and/or perborates (commercial sodium borate and/or perborate), usually in an amount of 10-20 percent by weight.

To support the activator component, optical brighteners may also be used, generally added in an amount of up to 1 percent by weight. To this end, the products available under the brand names Tinopal from CIBA-GEIGY AG have proven very suitable.

As additional additives, the following can be mentioned in particular; their use in the stated amounts is recommended for textile detergents for use with both hand and machine laundry;

#### 1) Enzymes

Various enzymes are available commercially for use in detergents, most of them acting specifically on certain types of soiling. The proteases that have proven especially suitable within the context of the present invention include in particular a mixture of savanase and esperase or alkalase as well as lipases and aminolytic enzymes such as Termamyl. These enzymes, which are generally used in a total amount of 0.5 - 8 percent by weight, are available from the company Novo Nordisk Industrie, Copenhagen.

#### 2) Carboxymethylcellulose

This substance keeps the dissolved particles of dirt in suspension in addition to contributing toward the rapid disintegration of detergents in water when the detergent is in the form of tablets, and can usually be added in an amount of up to 8 percent by weight.

#### 3) Zeolites

Zeolites are generally used in an amount of 5 - 40 percent by weight to increase the complexing effect for metal ions and alkaline earth metal ions in water. Suitable products are available commercially from Degussa.

4) Sodium carbonate and or sodium bicarbonate may be added in a total amount of 3 - 20 percent by weight to establish the desired pH of approximately 10-12, preferably 10-11.

5) Fiber protecting agents and anticorrosion agents: preferably sodium metasilicates and disilicates are preferably used as such in an amount of 5-15 percent by weight.

6) Coloring agents, e.g. ultramarine and perfume in suitable amounts, if desired

The most important advantage of the detergents according to this invention may be the complete absence of phosphates and chlorine as well as fillers. Due to the careful selection of components and the amounts used, not only is all environmental pollution, in particular water pollution, reduced to a tolerable extent

which is in compliance with the strict laws currently in effect, but also the product has such a concentrated detergent power that the amount added can be reduced to just a fraction of the amount recommended for so-called "concentrates". This also permits smaller packages and reduces the waste due to packaging.

Textile detergents are prepared easily from the components listed above. These components are mixed together very well without adding solvents of any type. It is advantageous for the production of the detergents according to this invention not to mix the individual components in an arbitrary sequence but instead to proceed as described below.

First a mixture A containing the amphoteric substances and, if any, the anionic surface-active substances together with the stabilizing agents and the agents to enhance detergent activity such as sodium carbonate and/or sodium bicarbonate, sodium silicate, carboxymethylcellulose and zeolite is prepared.

On the other hand, mixture B is prepared from the nonionic surface-active substances with stabilizing agents and agents to increase the detergent activities such as sodium carbonate and sodium bicarbonate, carboxymethylcellulose and zeolite.

The two mixtures A and B are then combined and blended with the remaining ingredients, namely borate and/or perborate, enzymes, citric acid, optical brighteners and optionally perfume and coloring agents.

The resulting free-flowing products generally tend to form lumps. Therefore, it is advisable to process the product into tablets which are used in a preferred dosage of 12 g/kg dry wash for machine laundry as well as hand laundry.

The powder mixture can be pressed to form tablets without any additional additives. This form has some advantages in comparison with free-flowing powder mixtures. It is much simpler to determine the dosage, and the packaging, e.g., in the blister packs that are popular today, is impermeable to air and moisture, save space and is environmentally friendly while also permitting the use of the detergent without coming in contact with the consumer. The components are selected so that the tablets disintegrate readily on coming in contact with water and dissolve immediately and completely in the wash water, even at low temperatures. The tablets preferably weigh 12 g and have a diameter of 30-32 mm and are added to advantage directly to the laundry in the washing machine drum. As shown by numerous studies, the agents according to this invention not only meet all the official requirements with regard to environmental protection and water conservation, but also they do not contain any harmful substances and they have proven to be completely safe for the health of humans and animals if the usual precautionary measures and dosage guidelines are maintained such as those which apply to working in the household in general.

These detergents are safe for use on all types of fabrics and fibers and protect even the most delicate textiles without attacking the textiles dyes and they also yield surprising removal of dirt and spots even in cold water but even more so at temperatures of 40-60°C. Comparative experiments with washing operations at 60°C and 95°C have shown that the laundry was not cleaned better or more rapidly by boiling.

Studies are underway regarding the disinfecting affect of the detergents according to this invention.

A recommended composition of the detergents is given below (in % by weight):

Washing-active substances (amphoteric)	5 - 15 preferably	8 - 12
Washing-active substances (nonionic)	5 - 20 “	10 - 14
Sodium borate and/or perborate	10 - 20	
Sodium carbonate and/or bicarbonate	3 - 20 “	1 - 15
Sodium metasilicate	0.1 - 5 “	0.5 - 4
Sodium disilicate	1 - 10 “	4 - 8
NTA Na <sup>3</sup>	0 - 10 “	3 - 10
CMC	0 - 7 “	1 - 4
Enzymes	0.5 - 8 “	1 - 5
Optical brighteners	0 - 1 “	0.1 - 0.3
Citric acid or citrate salts	1 - 20 “	5 - 15
Zeolites	5 - 40 “	5 - 20

All the amounts given are based on the weight of the finished mixture.

This invention also includes a new detergent for dishwashing machines based on the same principles. It is completely free of phosphate and chlorine and it has an excellent cleaning power while being extremely gentle on dishes and utensils (even those with a decorative finish).

A suitable composition includes in weight %:

Amphoteric surfactant	1 - 8 preferably	1 - 3
NTA Na <sup>3</sup>	20 - 30 “	10 - 25
Nonionic surfactant	5 - 15 “	2 - 8
Sodium metasilicate	5 - 30 “	7 - 25
Sodium carbonate	20 - 35 “	15 - 30
Citric acid	10 - 30 “	18 - 25
Enzymes	5 - 12 “	6 - 10
Sodium percarbonate	0 - 8	

This agent can also be pressed to advantage and without any further additives to form commercial tablets preferably weighing 8 g each which dissolve readily in water. One tablet is placed in the powder compartment of a dishwashing machine.

The following examples illustrate this invention in greater detail without restricting it in any way. For those skilled in the art it should be clear that additional additives can be added for special requirements.

## Example 1. Textile Detergent

The following ingredients were used (in kg) to produce 100 kg detergent powder:

Component	A	B	C
Amphoteric surfactants (Ampholak)	10		
Soap	5		
Sodium carbonate	6.25		
Sodium silicates	12.2		
CMC	1.3		
Zeolites	10.0		
Optical brightener	0.2		
NTA Na <sub>3</sub>	1.2		
Nonionic surfactants (Dobanol)	6.4		
Sodium carbonate		8.25	
CMC		1.3	
Zeolites		9.0	
Optical brightener		0.2	
NTA Na <sub>3</sub>		1.2	
Sodium perborate			8.0
Enzymes			7.0
Citric acids			12.5

Components A and B were also mixed well individually and then combined with the remaining ingredients of component C.

The results in free-flowing powder was pressed to form 12 g tablets in the usual way with a diameter of 30-32 mm. The dosage would depend on the prevailing hardness of the water but would in general amount to one tablet weighing 12 g for a kilogram of dry laundry.

Of course, the shape and weight of the pressed tablets can be varied as desired.

## Example 2

### Dishwashing detergent for automatic dishwashers

To produce 100 kg dishwashing detergent, the following ingredients were mixed together and the resulting homogeneous powder was pressed to form 8 g tablets having a diameter of 2.8 cm:

Amphoteric surfactant (Ampholak)	5 kg
Nonionic surface-active agent (Lutenol)	3 kg
Sodium carbonate	20 kg
Sodium percarbonate	5 kg
Sodium metasilicate	22 kg
Citric acid	20 kg
NTA Na <sub>3</sub>	20 kg
Enzymes	5 kg

The resulting tablets were packaged in airtight packages. When used, they are placed directly in the powder compartment of the dishwashing machine. The dosage depends on the instructions given by the machine manufacturer. Usually one tablet is sufficient for a normal wash cycle. It may be advisable to use an additional rinse agent in cases where water hardness is high but this is not necessary in most cases.

Patent Claims

1. Phosphate- and chlorine-free detergents and dishwashing agents based on washing-active, nonionic and/or ionic surface-active substances, characterized in that they also contain amphoteric surface-active substances, citric acid or the salts thereof.
2. Detergent and dishwashing agents according to Patent Claim 1, characterized in that they contain 5-15 percent by weight amphoteric substances and 5-30 percent by weight citric acid or the salts thereof.
3. Detergents for textiles according to Patent Claim 1 or 2, characterized by the following composition in percent by weight, based on the weight of the finished product:  

Washing-active substances (amphoteric)	5 - 15	preferably	8 - 12
Washing-active substances nonionic	5 - 20	"	10 - 14
Sodium borate and/or perborate	5 - 20		
Sodium carbonate and/or bicarbonate	3 - 20	"	1 - 15
Sodium metasilicate	0.1 - 5	"	0.5 - 4
Sodium disilicate	1 - 10	"	4 - 8
NTA Na <sup>3</sup>	0 - 10	"	3 - 10
CMC	0 - 7	"	1 - 4
Enzymes	0.5 - 8	"	1 - 5
Optical brighteners	0 - 1	"	0.1 - 0.3
Citric acid or citrate salts	1 - 20	"	5 - 15
Zeolites	5 - 40	"	5 - 20
4. Dishwashing product according to Patent Claim 1 or 2, characterized by the following composition in percent by weight, based on the weight of the finished product:  

Amphoteric surfactant	1 - 8	preferably	1 - 3
NTA Na <sup>3</sup>	20 - 30	"	10 - 25
Nonionic surfactant	5 - 15	"	2 - 8
Sodium metasilicate	5 - 30	"	7 - 25
Sodium carbonate	20 - 35	"	15 - 30
Citric acid	10 - 30	"	18 - 25
Enzymes	5 - 12	"	6 - 10
Sodium percarbonate	0 - 8		
5. Agent according to one of Claims 1 through 4 in tablet form.